Patent claims

1. An ion conducting composite membrane material consisting of a polymeric matrix filled with particles of cation, particularly proton, conducting, optionally modified, zirconium phosphate.

2. The membrane material according to claim 1 or 2 wherein the zirconium phosphate is a zirconium phosphate of the general formula $Zr(O_3POH)_{2-x}(O_3P\text{-}Ar)_x$, where Ar is a sulfoarylen group and $0 \leq x$.

3. The membrane material according to claim 1 or 2 wherein the zirconium phosphate is α-zirconium phosphate $Zr(O_3POH)_2$.

4. The membrane material according to claim 1 wherein the modified zirconium phosphate is a zirconium phosphate sulfoarylenphosphonate $Zr(O_3POH)_{2-x}(O_3P\text{-}Ar)_x$ wherein Ar is a sulfoarylen group and $0 < x \leq 2$.

5. The membrane material according to one of the claims 1-4 wherein the conductivity of the membrane material containing optionally modified zirconium phosphate is $>5 \times 10^{-4}$ S cm^{-1} at temperatures of 0 °C to 200 °C and a relative humidity of 100 %.

6. The membrane material according to one of the claims 1-5, wherein the conductivity of the membrane material containing zirconium phosphate, preferably a modified zirconium phosphate, especially zirconium phosphate sulfoarylenphosphonate, is $>10^{-2}$ S cm^{-1} at 70 °C and 95 % relative humidity.

7. The membrane material according to claim 1 wherein the polymeric matrix of the membrane material is that of an ionomer, especially of a proton conducting ionomer.

8. The membrane material according to one of the preceding claims wherein the polymeric matrix of the membrane material is at least one synthetic ionomer of the group consisting of perfluorosulfonic polymers, sulfonated polyvinylidenfluoride, sulfonated polyetherketones, sulfonated polybenzimidazoles, sulfonated polyphenylsulfones, sulfonated polysulfones and sulfonated polyethersulfones.

9. The membrane material according to one of the claims 2 and 4-8 wherein the zirconium phosphate sulfoarylenphosphonate contains specifically one or more phosphonate groups bonded to the zirconium atom.

10. The membrane material according to one of the claims 2 and 4-9 wherein the sulfoarylenphosphonate group is meta-sulfophenylenphosphonate.

11. The membrane material according to one of the preceding claims wherein optionally modified zirconium phosphate is of layered type.

12. The membrane material according to one of the preceding claims wherein the amount of optionally modified zirconium phosphate in the membrane material is 0,5 % – 70 %, preferably 5 % - 40 %, especially 10 % - 25 % by weight.

13. A method for the preparation of the proton conducting composite membrane material according to one of claims 1-12 based on the following steps:

a) preparation of a layered zirconium phosphate or modified zirconium phosphate,

b) preparation of a colloidal dispersion of the zirconium phosphate or modified zirconium phosphate in a suitable solvent or mixture of solvents,

c) transfer of the zirconium phosphate or modified zirconium phosphate particles from the said colloidal dispersion to a solution of a polymer,

d) forming membrane materials by using the mixture and eliminating the solvent.

14. The method for the preparation of the proton conducting composite membrane material according to claim 13 wherein the polymer is the ionomer of claim 7 or 8.

15. A method for the preparation of a proton conducting composite membrane material consisting of a synthetic ionomer of claims 7 or 8 filled with lamellar particles of α-zirconium phosphate based on the following steps:

a) exfoliation of α-zirconium phosphate in aqueous solution by intercalation - deintercalation of an alkyl amine,

b) dispersion of α-zirconium phosphate, obtained from the previous intercalation deintercalation process, into an organic solvent,

c) transfer of the exfoliated zirconium phosphate particles from the said colloidal dispersion to a solution of a polymer,

d) forming membrane materials by using the mixture and eliminating the solvent.

16. The methods for the preparation of the proton conducting composite membrane materials according to one of claims 13-15 wherein the mixture containing the polymer and the α-zirconium

phosphate or modified zirconium phosphate is obtained by mixing the ionomer solution with the colloidal dispersion of the layered α-zirconium phosphate or zirconium phosphate sulfoarylenphosphonate.

17. The method for the preparation of the proton conducting composite membrane material according to one of claims 13-16 wherein the colloidal dispersion of the α-zirconium phosphate or modified zirconium phosphate is obtained by using organic solvents selected from N, N'-dimethylformamide, N-methyl-2-pyrrolidone, dimethylsulfoxide, acetonitrile and alkanols, preferably N, N'-dimethylformamide and/or N-methyl-2-pyrrolidone, or their mixtures or water or mixtures of water and organic solvent.

18. The methods for the preparation of the proton conducting composite membrane materials of one of claims 13-17 wherein the ionomer solution and the colloidal dispersion are prepared in the same solvent or in different solvents, provided that the mixing of the solution with the dispersion does not cause colloid flocculation or ionomer precipitation.

19. The method for the preparation of the proton conducting composite membrane material according to claims 13-18 wherein the mixture containing the ionomer and the layered α-zirconium phosphate or zirconium phosphate sulfoarylenphosphonate is obtained by "phase transfer".

20. The methods for the preparation of the proton conducting composite membrane materials according to claims 13-18 wherein the solvent is removed from the polymer-colloid mixture by evaporation.

21. The methods for the preparation of the proton conducting composite membrane materials according to claims 13-18 wherein the solvent is removed from the polymer-colloid mixture by the use of a non-solvent, preferably water.

22. Use of the composite membrane materials of one of claims 1-12 as ionomeric membrane materials with high mechanical properties and/or decreasing methanol permeability.

23. Use of the composite membrane materials of one of claims 1-12 as ionomeric membrane materials with high overall performance in hydrogen, in indirect and in direct methanol fuel cells.

24. Use of the composite membrane materials containing α-zirconium phosphate according to one of claims 1-12 as ionomeric membrane materials with high overall performance in hydrogen and in indirect methanol fuel cells operating preferably at temperatures >80 °C.

25. Use of the composite membrane material according to one of claims 1-12 in direct methanol fuel cells.

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